

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

Attorney's Docket Number

05725.0555

U.S. Application No.

09/486558

International Application No.	International Filing Date	Priority Date Claimed
PCT/FR98/01591	July 20, 1998	September 1, 1997

Title of Invention:
DYEING COMPOSITION FOR KERATIN FIBRES

430 Rec'd PCT/PTO 29 FEB 2000

Applicant(s) For DO/EO/US:

Mireille MAUBRU and Marie-Pascale AUDOUSET

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A FIRST preliminary amendment.
- A SECOND or SUBSEQUENT preliminary amendment.
14. A substitute specification.
15. A change of power of attorney and/or address letter.
16. Other items or information:
 - a. Verified Small Entity Statement.
 - b. Copy of Notification of Missing Requirements.

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17. The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

CALCULATIONS

Search Report has been prepared by the EPO or JPO.....	\$840.00
International preliminary examination fee paid to USPTO (37 CFR 1.482).....	\$670.00
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....	\$760.00
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....	\$970.00
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4).....	\$ 96.00

ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 840.00

Surcharge of \$130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

Claims	Number Filed	Number Extra	Rate
Total Claims	25 -20=	5	X \$18.00 \$ 90.00
Independent Claims	1 - 3=		X \$78.00 \$
Multiple dependent claim(s) (if applicable)			+\$260.00 \$ 260.00

TOTAL OF ABOVE CALCULATIONS = \$1,190.00

Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)

SUBTOTAL = \$1,190.00

Processing fee of \$130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).

+

TOTAL NATIONAL FEE = \$1,190.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31).

\$40.00 per property + \$

TOTAL FEES ENCLOSED = \$1,190.00

Amount to be

refunded \$

charged \$

a. A check in the amount of \$1,190.00 to cover the above fees is enclosed.

b. Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 06-0916. A duplicate copy of this sheet is enclosed.

The Commissioner is hereby authorized to charge any other fees due under 37 C.F.R. §1.16 or §1.17 during the pendency of this application to our Deposit Account No. 06-0916.

SEND ALL CORRESPONDENCE TO:
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 Garrett & Dunner, L.L.P.
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 Washington, D.C. 20005-3315
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Ernest F. Chapman
 Reg. No. 25,961

Submitted: February 29, 2000

09/486558

13 APR 2000

PATENT

Attorney Docket No.: 5725.0555-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Stage of International)
Application No. PCT/FR98/01591 of:)
)
)
Mireille MAUBRU et al.)
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)
Serial No.: 09/486,558) Group Art Unit: Unassigned
)
)
PCT Filed: July 20, 1998) Examiner: Unassigned
)
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National Stage Entry: February 29, 2000)
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)
FOR: DYEING COMPOSITION FOR)
)
)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Attention: BOX PCT

Sir:

Prior to the examination of the above application, please amend the abstract, cancel claims 1 to 19 without prejudice or disclaimer and add new claims 20 to 47 as follows:

IN THE ABSTRACT:

Please delete the abstract and insert the new abstract, which is attached on a separate sheet.

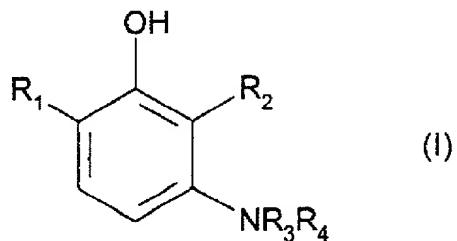
LAW OFFICES

FINNEGAN, HENDERSON,
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202-408-4000

IN THE CLAIMS:

--20. A composition for the oxidation dyeing of keratin fibers comprising:

- at least one oxidation base chosen from diaminopyrazoles, triaminopyrazoles, and acid-addition salts thereof;
- and at least one coupler chosen from halogenated meta-aminophenols of formula (I), and acid addition salts thereof:



in which:

- R₁ and R₂, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkoxy radical and a C₂-C₄ polyhydroxyalkoxy radical;

- R₃ and R₄, which are identical or different, are chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical and a C₁-C₄ monoaminoalkyl radical;
with the proviso that at least one of said radicals R₁ and R₂ is a halogen atom.

21. A composition according to Claim 20, wherein said keratin fibers are human keratin fibers.

22. A composition according to Claim 21, wherein said human keratin fibers are human hair.

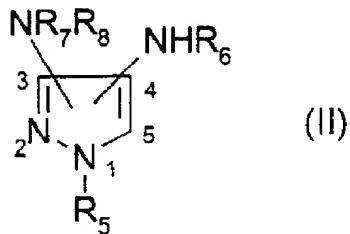
23. A composition according to Claim 20, wherein said composition is in a medium suitable for dyeing.

24. A composition according to Claim 20, wherein said halogen atoms are chosen from chlorine, bromine, iodine and fluorine.

25. A composition according to Claim 20, wherein said halogenated meta-aminophenols of formula (I) are chosen from 3-amino-6-chlorophenol, 3-amino-6-bromophenol, 3-(β -aminoethyl)amino-6-chlorophenol, 3-(β -hydroxyethyl)amino-6-chlorophenol and 3-amino-2-chloro-6-methylphenol, and acid addition salts thereof.

26. A composition according to Claim 20, wherein said diaminopyrazoles are chosen from:

a) diaminopyrazoles of formula (II), and acid addition salts thereof:

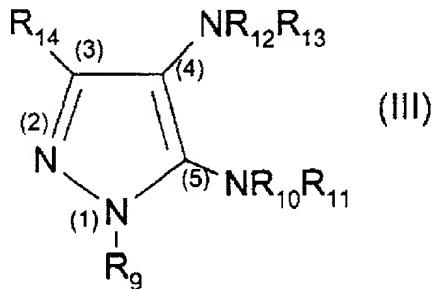


in which:

- R_5 is chosen from a hydrogen atom, a C_1 - C_6 alkyl radical, a C_2 - C_4 hydroxyalkyl radical, a benzyl radical, a phenyl radical, a benzyl radical substituted with a halogen atom, a C_1 - C_4 alkyl radical or C_1 - C_4 alkoxy radical, or R_5 forms, with the nitrogen atom of the group NR_7R_8 in position 5, a hexahdropyridazine or tetrahydropyrazole heterocycle which is optionally monosubstituted with a C_1 - C_4 alkyl group;
- R_6 and R_7 which are identical or different, are chosen from a hydrogen atom, a C_1 - C_4 alkyl radical, a C_2 - C_4 hydroxyalkyl radical, a benzyl radical and a phenyl radical;
- R_8 is chosen from a hydrogen atom, a C_1 - C_6 alkyl radical and a C_2 - C_4 hydroxyalkyl radical;

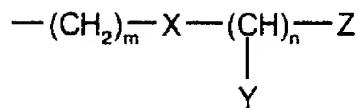
with the proviso that R₆ is a hydrogen atom when R₅ either is a substituted benzyl radical or forms a heterocycle with the nitrogen atom of the group NR₇R₈ in position 5; and

b) diaminopyrazoles of formula (III), and acid addition salts thereof:



in which:

- R₉, R₁₀, R₁₁, R₁₂ and R₁₃, which are identical or different, are chosen from a hydrogen atom; a linear or branched C₁-C₆ alkyl radical; a C₂-C₄ hydroxyalkyl radical; a C₂-C₄ aminoalkyl radical; a phenyl radical; a phenyl radical substituted with a halogen atom or a C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, trifluoromethyl, amino or C₁-C₄ alkylamino radical; a benzyl radical; a benzyl radical substituted with a halogen atom or with a C₁-C₄ alkyl, C₁-C₄ alkoxy, methylenedioxy or amino radical; and a radical



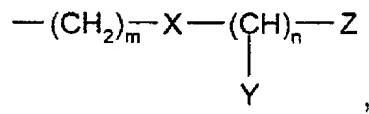
in which m and n are integers, which are identical or different, ranging from 1 to 3 inclusive, X is chosen from an oxygen atom and an NH group, Y is chosen from a hydrogen atom and a methyl radical, and Z is chosen from a methyl radical and a group OR or NRR' in which R and R', which are identical or different, are chosen from a hydrogen atom, a methyl radical and an ethyl radical, with the proviso that when R₁₀ is a hydrogen atom, then R₁₁ can also be an amino or C₁-C₄ alkylamino radical,

- R₁₄ is chosen from a linear or branched C₁-C₆ alkyl radical; a C₁-C₄ hydroxyalkyl radical; a C₁-C₄ aminoalkyl radical; a (C₁-C₄)alkylamino(C₁-C₄)alkyl radical; a di(C₁-C₄)alkylamino(C₁-C₄)alkyl radical; a hydroxy(C₁-C₄)alkylamino(C₁-C₄)alkyl radical; a (C₁-C₄)alkoxymethyl radical; a phenyl radical; a phenyl radical substituted with a halogen atom or with a C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, trifluoromethyl, amino or C₁-C₄ alkylamino radical; a benzyl radical; a benzyl radical substituted with a halogen atom or with a C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, trifluoromethyl, amino or C₁-C₄ alkylamino radical; a heterocycle chosen from thiophene, furan and pyridine; and a radical -(CH₂)_p-O-(CH₂)_q-OR", in which p and q are integers, which are identical or

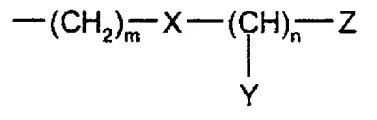
different, ranging from 1 to 3 inclusive, and R" is chosen from a hydrogen atom and a methyl radical;

with the provisos that, in formula (III),

- at least one of the radicals R₁₀, R₁₁, R₁₂ and R₁₃ is a hydrogen atom;
- when R₁₀, or R₁₂, respectively, is a substituted or unsubstituted phenyl radical, or a benzyl radical or a radical



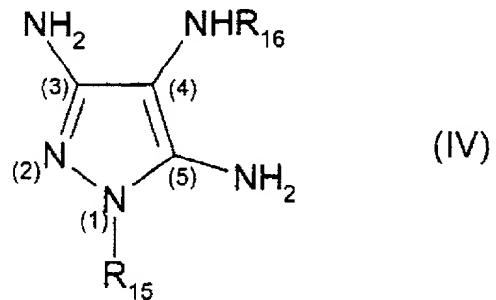
then R₁₁, or R₁₃, respectively, is not a substituted or unsubstituted phenyl radical, or a benzyl radical or a radical



- when R₁₂ and R₁₃ simultaneously represent a hydrogen atom, then R₉ can form, with R₁₀ and R₁₁, a hexahydropyrimidine or tetrahydroimidazole heterocycle which is optionally substituted with a C₁-C₄ alkyl or 1,2,4-tetrazole radical;
- when R₁₀, R₁₁, R₁₂ and R₁₃ represent a hydrogen atom or a C₁-C₆ alkyl radical, then R₉ or R₁₄ can also represent a 2-, 3- or 4-pyridyl, 2- or 3-thienyl or 2- or 3-furyl

heterocyclic residue which is optionally substituted with a methyl radical or a cyclohexyl radical.

27. A composition according to Claim 20, wherein said triaminopyrazoles are chosen from compounds of formula (IV), and acid addition salts thereof:



in which:

- R₁₅ and R₁₆, which are identical or different, are chosen from a hydrogen atom, a C₁-C₄ alkyl and a C₂-C₄ hydroxyalkyl radical.

28. A composition according to Claim 26, wherein said diaminopyrazoles of formula (II) are chosen from:

- 4,5-diamino-1-(4'-methoxybenzyl)pyrazole,
- 4,5-diamino-1-(4'-methylbenzyl)pyrazole,

- 4,5-diamino-1-(4'-chlorobenzyl)pyrazole,
- 4,5-diamino-1-(3'-methoxybenzyl)pyrazole,
- 4-amino-1-(4'-methoxybenzyl)-5-methylaminopyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-(4'-methoxybenzyl)pyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-methylpyrazole,
- 4-amino-(3)5-methylaminopyrazole,
- 3-(5)4-diaminopyrazole,
- 4,5-diamino-1-methylpyrazole,
- 4,5-diamino-1-benzylpyrazole,
- 3-amino-4,5,7,8-tetrahydropyrazolo{1,5-a}pyrimidine,
- 7-amino-2,3-dihydro-1H-imidazolo{1,2-b}pyrazole,
- 3-amino-8-methyl-4,5,7,8-tetrahydropyrazolo{1,5-a}pyrimidine,
and acid addition salts thereof.

29. A composition according to Claim 26, wherein said diaminopyrazoles of formula (III) are chosen from:

- 1-benzyl-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methoxyphenyl)pyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methylphenyl)pyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-(3'-methylphenyl)pyrazole,
- 4,5-diamino-3-methyl-1-isopropylpyrazole,

- 4,5-diamino-3-(4'-methoxyphenyl)-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
- 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-tert-butylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-phenylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-(2'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-hydroxymethyl-1-(3'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-hydroxymethyl-1-(4'-methoxyphenyl)pyrazole,
- 1-benzyl-4,5-diamino-3-hydroxymethylpyrazole,
- 4,5-diamino-3-methyl-1-(2'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-methyl-1-(3'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-methyl-1-(4'-methoxyphenyl)pyrazole,
- 3-aminomethyl-4,5-diamino-1-methylpyrazole,
- 3-aminomethyl-4,5-diamino-1-ethylpyrazole,
- 3-aminomethyl-4,5-diamino-1-isopropylpyrazole,
- 3-aminomethyl-4,5-diamino-1-tert-butylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-isopropylpyrazole,

- 4,5-diamino-3-dimethylaminomethyl-1-tert-butylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-ethylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-isopropylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-tert-butylpyrazole,
- 4,5-diamino-3-methylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-methylaminomethyl-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-methylaminomethylpyrazole,
- 1-tert-butyl-4,5-diamino-3-methylaminomethylpyrazole,
- 4,5-diamino-3- $\{(\beta\text{-hydroxyethyl})\text{aminomethyl}\}$ -1-methylpyrazole,
- 4,5-diamino-3- $\{(\beta\text{-hydroxyethyl})\text{aminomethyl}\}$ -1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3- $\{(\beta\text{-hydroxyethyl})\text{aminomethyl}\}$ pyrazole,
- 1-tert-butyl-4,5-diamino-3- $\{(\beta\text{-hydroxyethyl})\text{aminomethyl}\}$ pyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1,3-dimethylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-isopropyl-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-ethyl-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-tert-butyl-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-phenyl-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-(2-methoxyphenyl)-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-(3-methoxyphenyl)-3-methylpyrazole,

- 4-amino-5-(β -hydroxyethyl)amino-1-(4-methoxyphenyl)-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-benzyl-3-methylpyrazole,
- 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,
- 4-amino-1-tert-butyl-3-methyl-5-methylaminopyrazole,
- 4,5-diamino-1,3-dimethylpyrazole,
- 4,5-diamino-3-tert-butyl-1-methylpyrazole,
- 4,5-diamino-1-tert-butyl-3-methylpyrazole,
- 4,5-diamino-1-methyl-3-phenylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-phenylpyrazole,
- 4,5-diamino-1-methyl-3-(2'-chlorophenyl)pyrazole,
- 4,5-diamino-1-methyl-3-(4'-chlorophenyl)pyrazole,
- 4,5-diamino-1-methyl-3-(3'-trifluoromethylphenyl)pyrazole,
- 4,5-diamino-1,3-diphenylpyrazole,
- 4,5-diamino-3-methyl-1-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-phenylaminopyrazole,
- 4-amino-1-ethyl-3-methyl-5-phenylaminopyrazole,
- 4-amino-1,3-dimethyl-5-methylaminopyrazole,
- 4-amino-3-methyl-1-isopropyl-5-methylaminopyrazole,
- 4-amino-3-isobutoxymethyl-1-methyl-5-methylaminopyrazole,

- 4-amino-3-methoxyethoxymethyl-1-methyl-5-methylaminopyrazole,
- 4-amino-3-hydroxymethyl-1-methyl-5-methylaminopyrazole,
- 4-amino-1,3-diphenyl-5-phenylaminopyrazole,
- 4-amino-3-methyl-5-methylamino-1-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
- 5-amino-3-methyl-4-methylamino-1-phenylpyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-(4'-chlorophenyl)pyrazole,
- 5-amino-3-ethyl-1-methyl-4-(N,N-methylphenyl)aminopyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-phenylpyrazole,
- 5-amino-3-ethyl-4-(N,N-methylphenyl)aminopyrazole,
- 5-amino-4-(N,N-methylphenyl)amino-3-phenylpyrazole,
- 5-amino-4-(N,N-methylphenyl)amino-3-(4'-methylphenyl)pyrazole,
- 5-amino-3-(4'-chlorophenyl)-4-(N,N-methylphenyl)aminopyrazole,
- 5-amino-3-(4'-methoxyphenyl)-4-(N,N-methylphenyl)aminopyrazole,
- 4-amino-5-methylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-(4'-methylphenyl)pyrazole,
- 4-amino-3-phenyl-5-propylaminopyrazole,
- 4-amino-5-butylamino-3-phenylpyrazole,
- 4-amino-3-phenyl-5-phenylaminopyrazole,
- 4-amino-5-benzylamino-3-phenylpyrazole,

- 4-amino-5-(4'-chlorophenyl)amino-3-phenylpyrazole,
- 4-amino-3-(4'-chlorophenyl)-5-phenylaminopyrazole,
- 4-amino-3-(4'-methoxyphenyl)-5-phenylaminopyrazole,
- 1-(4'-chlorobenzyl)-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,
- 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

and acid addition salts thereof.

30. A composition according to Claim 29, wherein said diaminopyrazoles of formula (III) are chosen from:

- 4,5-diamino-1,3-dimethylpyrazole,
- 4,5-diamino-3-methyl-1-phenylpyrazole,
- 4,5-diamino-1-methyl-3-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
- 1-benzyl-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-3-tert-butyl-1-methylpyrazole,
- 4,5-diamino-1-tert-butyl-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,

- 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4,5-diamino-3-methyl-1-isopropylpyrazole,
- 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,
and acid addition salts thereof.

31. A composition according to Claim 27 wherein said triaminopyrazoles of formula (IV) are chosen from 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole, and acid addition salts thereof.

32. A composition according to Claim 20, wherein said at least one oxidation base is present in an amount ranging from 0.0005 to 12% by weight relative to the total weight of the composition.

33. A composition according to Claim 32, wherein said at least one oxidation base is present in an amount ranging from 0.005 to 6% by weight relative to the total weight of the composition.

34. A composition according to Claim 20, wherein said at least one coupler is present in an amount ranging from 0.0001 to 5% by weight relative to the total weight of the composition.

35. A composition according to Claim 34, wherein said at least one coupler is present in an amount ranging from 0.005 to 3% by weight relative to the total weight of the composition.

36. A composition according to Claim 20, wherein said acid addition salts are chosen from hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

37. A composition according to Claim 23, wherein said medium suitable for dyeing or support comprises water or a mixture of water and at least one organic solvent.

38. A composition according to Claim 37, wherein said at least one organic solvent is chosen from C₁-C₄ lower alkanols, glycerol, glycols and glycol ethers, aromatic alcohols and similar products.

39. A composition according to Claim 20, wherein said composition has a pH ranging from 3 to 12.

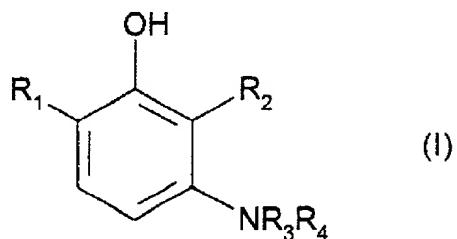
40. A composition according to Claim 20, wherein said composition is in the form of a liquid, a cream, or a gel.

41. A composition according to Claim 40, wherein said composition is in the form of a liquid, a cream, a gel, or in any other form suitable for dyeing human hair.

42. A method for dyeing keratin fibers, comprising:

(a) applying to said keratin fibers at least one dye composition, which comprises

- at least one oxidation base chosen from diaminopyrazoles, triaminopyrazoles, and acid-addition salts thereof;
- and at least one coupler chosen from halogenated meta-aminophenols of formula (I), and acid addition salts thereof:



in which:

- R₁ and R₂, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkoxy radical and a C₂-C₄ polyhydroxyalkoxy radical;

- R₃ and R₄, which are identical or different, are chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical and a C₁-C₄ monoaminoalkyl radical;

with the proviso that at least one of said radicals R₁ and R₂ is a halogen atom;

and

(b) developing a color at an acidic, neutral or alkaline pH with the aid of an oxidizing agent, wherein said oxidizing agent is added to said at least one dye composition at the time of application of said composition, or wherein said oxidizing agent is present in an oxidizing composition, and wherein said oxidizing composition is applied simultaneously or sequentially with said at least one dye composition.

43. A method according to Claim 42, wherein said keratin fibers are human keratin fibers.

44. A method according to Claim 43, wherein said human keratin fibers are human hair.

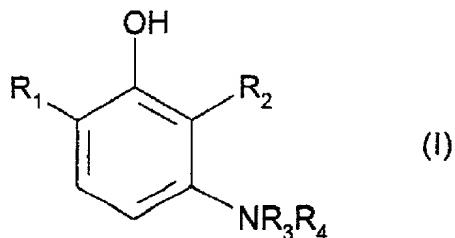
45. A method according to Claim 42, wherein said oxidizing agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, and peracids.

46. A method according to Claim 45, wherein said persalts are chosen from perborates, percarbonates and persulphates.

47. A multi-compartment kit for dyeing keratin fibers, comprising at least two compartments, wherein one compartment comprises an oxidizing composition,

and another compartment comprises a composition for the oxidation dyeing of keratin fibers, said composition for the oxidation dyeing of keratin fibers comprising:

- at least one oxidation base chosen from diaminopyrazoles, triaminopyrazoles, and acid-addition salts thereof;
- and at least one coupler chosen from halogenated meta-aminophenols of formula (I), and acid addition salts thereof:



in which:

- R₁ and R₂, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkoxy radical and a C₂-C₄ polyhydroxyalkoxy radical;

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- R₃ and R₄, which are identical or different, are chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical and a C₁-C₄ monoaminoalkyl radical;
with the proviso that at least one of said radicals R₁ and R₂ is a halogen atom.--

REMARKS

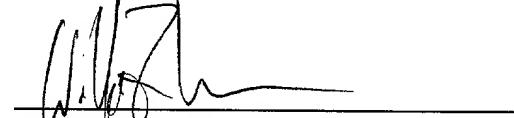
Claims 1 through 19 have been canceled and rewritten as new claims 20 through 47 to more particularly point out and distinctly claim that which Applicants consider to be their invention. Applicants have also replaced the abstract. No new matter has been added by these amendments. Applicants now await an action on the merits.

Please grant any extensions of time required to enter this Preliminary Amendment and charge any additional required fees to our deposit account Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

By:



William Z. Nakhleh
Reg. No. 42,924

Dated: April 13, 2000

ABSTRACT

The present invention relates to a composition for the oxidation dyeing of keratin fibers, in particular human keratin fibers, such as the hair, having at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles, in combination with at least one meta-aminophenol which is halogenated ortho to the phenol, as coupler, and to the dyeing process using this composition with an oxidizing agent.

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COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,
COMPRISING A DIAMINOPYRAZOLE OR A TRIAMINOPYRAZOLE AND
A HALOGENATED META-AMINOPHENOL, AND DYEING PROCESS

5 The present invention relates to a composition for the oxidation dyeing of keratin fibres, in particular human keratin fibres such as the hair, comprising at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles, in combination 10 with at least one meta-aminophenol which is halogenated ortho to the phenol, as coupler, and to the dyeing process using this composition with an oxidizing agent.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions 15 containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols or heterocyclic compounds such as pyrazole derivatives, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation 20 bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by means of a process of oxidative condensation.

It is also known that the shades obtained 25 with oxidation bases can be varied by combining them with suitably selected couplers or coloration

modifiers, the latter possibly being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

5 The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained by means of these oxidation dyes must moreover satisfy
10 a certain number of requirements. Thus, it must have no toxicological drawbacks, it must allow shades to be obtained in the desired intensity and it must satisfactorily withstand external agents (light, bad weather, washing, permanent-waving, perspiration or
15 rubbing).

The dyes must also be able to cover white hair, and, lastly, they must be as unselective as possible, i.e. they must allow only the smallest possible differences in colour along the same keratin
20 fibre, which may in fact be differently sensitized (i.e. damaged) between its tip and its root.

Compositions for the oxidation dyeing of keratin fibres, containing pyrazole derivatives such as 4,5-diaminopyrazoles, 3,4-diaminopyrazoles or 3,4,5-triaminopyrazoles as oxidation base, in combination with couplers conventionally used for oxidation dyeing,

such as, for example, meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers such as, for example, indole derivatives, have already been proposed, in particular in German patent 5 applications DE 3 843 892, DE 4 234 887, DE 4 234 886, DE 4 234 885 and DE 195 43 988. However, such compositions are not entirely satisfactory, in particular as regards the fastness of the colorations obtained with regard to the various attacking factors 10 to which the hair may be subjected, and in particular with regard to perspiration.

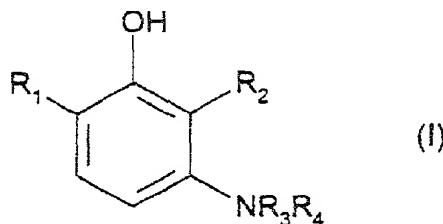
However, the Applicant has now discovered that it is possible to obtain novel powerful dyes that are particularly resistant to the various attacking 15 factors to which the hair may be subjected, by combining, as oxidation base, at least one diaminopyrazole and/or at least one triaminopyrazole and, as coupler, a meta-aminophenol halogenated in a position ortho to the phenol.

20 This discovery forms the basis of the present invention.

A first subject of the invention is thus a composition for the oxidation dyeing of keratin fibres and in particular human keratin fibres such as the 25 hair, characterized in that it comprises, in a medium which is suitable for dyeing:

- at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles;
- and at least one coupler chosen from the halogenated meta-aminophenols of formula (I) below, and the

5 addition salts thereof with an acid:



in which:

- R₁ and R₂, which may be identical or different, represent a hydrogen atom, a halogen atom such as 10 chlorine, bromine, iodine or fluorine, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkoxy radical or a C₂-C₄ polyhydroxyalkoxy radical;
- 15 - R₃ and R₄, which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical or a C₁-C₄ monoaminoalkyl radical; it being understood that at least one of the radicals R₁ 20 and R₂ represents a halogen atom.

The oxidation dye composition in accordance with the invention makes it possible to obtain intense colorations in varied shades, which are relatively

unselective and which have excellent properties of resistance both with respect to atmospheric agents such as light and bad weather, and with respect to perspiration and the various treatments to which the hair may be subjected (shampooing, permanent-waving).

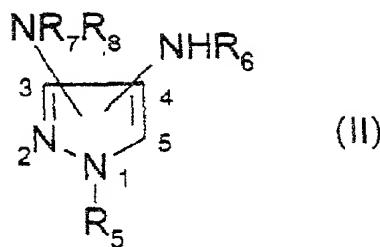
These properties are particularly noteworthy especially as regards the resistance of the colorations with respect to perspiration.

Among the C₁-C₄ alkyl and C₁-C₄ alkoxy radicals
10 of the compounds of formula (I) above, mention may be
made in particular of the methyl, ethyl, propyl,
methoxy and ethoxy radicals.

Among the halogenated meta-aminophenols of formula (I), mention may be made more particularly of 15 3-amino-6-chlorophenol, 3-amino-6-bromophenol, 3-(β -aminoethyl)amino-6-chlorophenol, 3-(β -hydroxyethyl)-amino-6-chlorophenol and 3-amino-2-chloro-6-methylphenol, and the addition salts thereof with an acid.

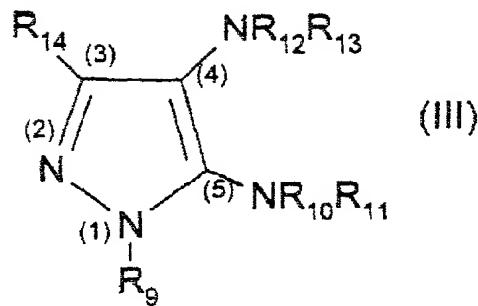
20 Among the diaminopyrazoles which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of:

a) the diaminopyrazoles of formula (II) below, and the
25 addition salts thereof with an acid:



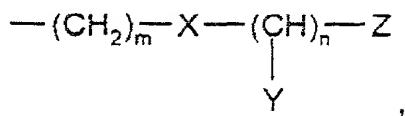
in which:

- R₅ represents a hydrogen atom, a C₁-C₆ alkyl radical, a C₂-C₄ hydroxyalkyl radical, a benzyl radical, a phenyl radical, a benzyl radical substituted with a halogen atom or with a C₁-C₄ alkyl or C₁-C₄ alkoxy group, or forms, with the nitrogen atom of the group NR₇R₈ in position 5, a hexahdropyridazine or tetrahydropyrazole heterocycle which is optionally monosubstituted with a C₁-C₄ alkyl group;
- R₆ and R₇ which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, a C₂-C₄ hydroxyalkyl radical, a benzyl radical or a phenyl radical;
- R₈ represents a hydrogen atom, or a C₁-C₆ alkyl or C₂-C₄ hydroxyalkyl radical; with the proviso that R₆ represents a hydrogen atom when R₅ represents a substituted benzyl radical or forms a heterocycle with the nitrogen atom of the group NR₇R₈ in position 5;
- b) the diaminopyrazoles of formula (III) below, and the addition salts thereof with an acid:



in which:

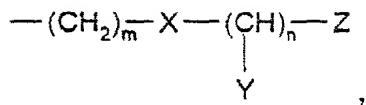
- R_9 , R_{10} , R_{11} , R_{12} and R_{13} , which may be identical or different, represent a hydrogen atom; a linear or 5 branched C_1 - C_6 alkyl radical; a C_2 - C_4 hydroxyalkyl radical; a C_2 - C_4 aminoalkyl radical; a phenyl radical; a phenyl radical substituted with a halogen atom or a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, nitro, trifluoromethyl, amino or C_1 - C_4 alkylamino radical; a benzyl radical; a benzyl 10 radical substituted with a halogen atom or with a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, methylenedioxy or amino radical; or a radical



- in which m and n are integers, which may be identical 15 or different, between 1 and 3 inclusive, X represents an oxygen atom or an NH group, Y represents a hydrogen atom or a methyl radical, and Z represents a methyl radical, a group OR or NRR' in which R and R' , which may be identical or different, denote a hydrogen atom, 20 a methyl radical or an ethyl radical,

it being understood that when R_{10} represents a hydrogen atom, then R_{11} can also represent an amino or C_1 - C_4 alkylamino radical,

- R_{14} represents a linear or branched C_1 - C_6 alkyl radical; a C_1 - C_4 hydroxyalkyl radical; a C_1 - C_4 aminoalkyl radical; a $(C_1$ - $C_4)$ alkylamino(C_1 - $C_4)$ alkyl radical; a di(C_1 - $C_4)$ alkylamino(C_1 - $C_4)$ alkyl radical; a hydroxy(C_1 - $C_4)$ alkylamino(C_1 - $C_4)$ alkyl radical; a $(C_1$ - $C_4)$ alkoxyethyl radical; a phenyl radical; a phenyl radical substituted 10 with a halogen atom or with a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, nitro, trifluoromethyl, amino or C_1 - C_4 alkylamino radical; a benzyl radical; a benzyl radical substituted with a halogen atom or with a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, nitro, trifluoromethyl, amino or C_1 - C_4 alkylamino radical; a heterocycle chosen from thiophene, furan and pyridine, or alternatively a radical $-(CH_2)_p-O-(CH_2)_q-$ 15 OR'', in which p and q are integers, which may be identical or different, between 1 and 3 inclusive, and R'' represents a hydrogen atom or a methyl radical,
- 20 it being understood that, in formula (III) above,
 - at least one of the radicals R_{10} , R_{11} , R_{12} and R_{13} represents a hydrogen atom,
 - when R_{10} , or R_{12} , respectively, represents a substituted or unsubstituted phenyl radical, or a
- 25 benzyl radical or a radical

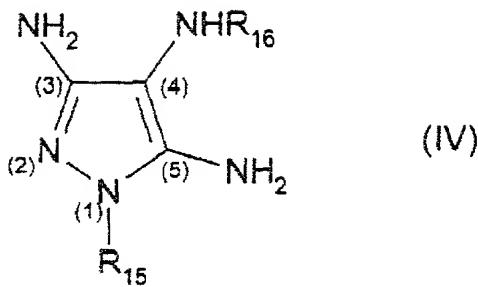


then R_{11} , or R_{13} , respectively, cannot represent any of these three radicals,

5 - when R_{12} and R_{13} simultaneously represent a hydrogen atom, then R_9 can form, with R_{10} and R_{11} , a hexahydropyrimidine or tetrahydroimidazole heterocycle which is optionally substituted with a $\text{C}_1\text{-}\text{C}_4$ alkyl or 1,2,4-tetrazole radical,

10 - when R_{10} , R_{11} , R_{12} and R_{13} represent a hydrogen atom or a $\text{C}_1\text{-}\text{C}_6$ alkyl radical, then R_9 or R_{14} can also represent a 2-, 3- or 4-pyridyl, 2- or 3-thienyl or 2- or 3-furyl heterocyclic residue which is optionally substituted with a methyl radical or alternatively a cyclohexyl radical.

15 Among the triaminopyrazoles which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds of formula (IV) below, and the addition salts thereof with an acid:



in which:

- R_{15} and R_{16} , which may be identical or different, represent a hydrogen atom or a C_1 - C_4 alkyl or C_2 - C_4 hydroxyalkyl radical.

Among the diaminopyrazoles of formula (II) above, mention may be made more particularly of 4,5-diamino-1-(4'-methoxybenzyl)pyrazole, 4,5-diamino-1-(4'-methylbenzyl)pyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1-(3'-methoxybenzyl)pyrazole, 4-amino-1-(4'-methoxybenzyl)-5-methylaminopyrazole, 4-amino-5-(β -hydroxyethyl)amino-1-(4'-methoxybenzyl)pyrazole, 4-amino-5-(β -hydroxyethyl)amino-1-methylpyrazole, 4-amino-5-(3)-5-methylaminopyrazole, 3-(5)4-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-benzylpyrazole, 3-amino-4,5,7,8-tetrahydropyrazolo[1,5-a]pyrimidine, 7-amino-2,3-dihydro-1H-imidazolo[1,2-b]pyrazole and 3-amino-8-methyl-4,5,7,8-tetrahydropyrazolo[1,5-a]pyrimidine, and the addition salts thereof with an acid.

The diaminopyrazoles of formula (III) are known compounds which can be prepared according to the synthetic process as described, for example, in French patent application FR-A-2 733 749.

5 Among the diaminopyrazoles of formula (III) above, mention may be made more particularly of:

- 1-benzyl-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methoxyphenyl)-pyrazole,
- 10 - 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methylphenyl)-pyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-(3'-methylphenyl)-pyrazole,
- 4,5-diamino-3-methyl-1-isopropylpyrazole,
- 15 - 4,5-diamino-3-(4'-methoxyphenyl)-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
- 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
- 20 - 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-tert-butylypyrazole,
- 4,5-diamino-3-hydroxymethyl-1-phenylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-(2'-methoxyphenyl)-pyrazole,
- 25 - 4,5-diamino-3-hydroxymethyl-1-(3'-methoxyphenyl)-pyrazole,

- 4,5-diamino-3-hydroxymethyl-1-(4'-methoxyphenyl)-pyrazole,
- 1-benzyl-4,5-diamino-3-hydroxymethylpyrazole,
- 4,5-diamino-3-methyl-1-(2'-methoxyphenyl)pyrazole,
- 5 - 4,5-diamino-3-methyl-1-(3'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-methyl-1-(4'-methoxyphenyl)pyrazole,
- 3-aminomethyl-4,5-diamino-1-methylpyrazole,
- 3-aminomethyl-4,5-diamino-1-ethylpyrazole,
- 3-aminomethyl-4,5-diamino-1-isopropylpyrazole,
- 10 - 3-aminomethyl-4,5-diamino-1-tert-butylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-ethylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-isopropylpyrazole,
- 15 - 4,5-diamino-3-dimethylaminomethyl-1-tert-butylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-ethylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-isopropylpyrazole,
- 20 - 4,5-diamino-3-ethylaminomethyl-1-tert-butylpyrazole,
- 4,5-diamino-3-methylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-methylaminomethyl-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-methylaminomethylpyrazole,
- 1-tert-butyl-4,5-diamino-3-methylaminomethylpyrazole,
- 25 - 4,5-diamino-3-[(β -hydroxyethyl)aminomethyl]-1-methylpyrazole,

- 4,5-diamino-3-[(β -hydroxyethyl)aminomethyl]-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-[(β -hydroxyethyl)aminomethyl]-pyrazole,
- 5 - 1-tert-butyl-4,5-diamino-3-[(β -hydroxyethyl)aminomethyl]pyrazole,
 - 4-amino-5- (β -hydroxyethyl) amino-1,3-dimethylpyrazole,
 - 4-amino-5- (β -hydroxyethyl) amino-1-isopropyl-3-methyl-pyrazole,
- 10 - 4-amino-5- (β -hydroxyethyl) amino-1-ethyl-3-methyl-pyrazole,
 - 4-amino-5- (β -hydroxyethyl) amino-1-tert-butyl-3-methylpyrazole,
 - 4-amino-5- (β -hydroxyethyl) amino-1-phenyl-3-methyl-pyrazole,
- 15 - 4-amino-5- (β -hydroxyethyl) amino-1- (2-methoxyphenyl) -3-methylpyrazole,
 - 4-amino-5- (β -hydroxyethyl) amino-1- (3-methoxyphenyl) -3-methylpyrazole,
- 20 - 4-amino-5- (β -hydroxyethyl) amino-1- (4-methoxyphenyl) -3-methylpyrazole,
 - 4-amino-5- (β -hydroxyethyl) amino-1-benzyl-3-methyl-pyrazole,
 - 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,

- 4-amino-1-tert-butyl-3-methyl-5-methylaminopyrazole,
- 4,5-diamino-1,3-dimethylpyrazole,
- 4,5-diamino-3-tert-butyl-1-methylpyrazole,
- 4,5-diamino-1-tert-butyl-3-methylpyrazole,
- 5 - 4,5-diamino-1-methyl-3-phenylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-phenylpyrazole,
- 4,5-diamino-1-methyl-3-(2'-chlorophenyl)pyrazole,
- 4,5-diamino-1-methyl-3-(4'-chlorophenyl)pyrazole,
- 10 - 4,5-diamino-1-methyl-3-(3'-trifluoromethylphenyl)-pyrazole,
- 4,5-diamino-1,3-diphenylpyrazole,
- 4,5-diamino-3-methyl-1-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-phenylaminopyrazole,
- 15 - 4-amino-1-ethyl-3-methyl-5-phenylaminopyrazole,
- 4-amino-1,3-dimethyl-5-methylaminopyrazole,
- 4-amino-3-methyl-1-isopropyl-5-methylaminopyrazole,
- 4-amino-3-isobutoxymethyl-1-methyl-5-methylamino-pyrazole,
- 20 - 4-amino-3-methoxyethoxymethyl-1-methyl-5-methylamino-pyrazole,
- 4-amino-3-hydroxymethyl-1-methyl-5-methylamino-pyrazole,
- 4-amino-1,3-diphenyl-5-phenylaminopyrazole,
- 25 - 4-amino-3-methyl-5-methylamino-1-phenylpyrazole,

- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
- 5-amino-3-methyl-4-methylamino-1-phenylpyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-(4'-chlorophenyl)pyrazole,
- 5 - 5-amino-3-ethyl-1-methyl-4-(N,N-methylphenyl)amino-pyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-phenyl-pyrazole,
- 5-amino-3-ethyl-4-(N,N-methylphenyl)aminopyrazole,
- 10 - 5-amino-4-(N,N-methylphenyl)amino-3-phenylpyrazole,
- 5-amino-4-(N,N-methylphenyl)amino-3-(4'-methyl-phenyl)pyrazole,
- 5-amino-3-(4'-chlorophenyl)-4-(N,N-methylphenyl)-aminopyrazole,
- 15 - 5-amino-3-(4'-methoxyphenyl)-4-(N,N-methylphenyl)-aminopyrazole,
- 4-amino-5-methylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-(4'-methylphenyl)pyrazole,
- 20 - 4-amino-3-phenyl-5-propylaminopyrazole,
- 4-amino-5-butylamino-3-phenylpyrazole,
- 4-amino-3-phenyl-5-phenylaminopyrazole,
- 4-amino-5-benzylamino-3-phenylpyrazole,
- 4-amino-5-(4'-chlorophenyl)amino-3-phenylpyrazole,
- 25 - 4-amino-3-(4'-chlorophenyl)-5-phenylaminopyrazole,
- 4-amino-3-(4'-methoxyphenyl)-5-phenylaminopyrazole,

- 1-(4'-chlorobenzyl)-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,
- 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

5 and the addition salts thereof with an acid.

5 and the addition salts thereof with an acid.

Among these diaminopyrazoles of formula (III) above, the ones more particularly preferred are:

- 4,5-diamino-1,3-dimethylpyrazole,
- 4,5-diamino-3-methyl-1-phenylpyrazole,
- 10 - 4,5-diamino-1-methyl-3-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
- 1-benzyl-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-3-tert-butyl-1-methylpyrazole,
- 4,5-diamino-1-tert-butyl-3-methylpyrazole,
- 15 - 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
- 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
- 20 - 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4,5-diamino-3-methyl-1-isopropylpyrazole,
- 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

Among the triaminopyrazoles of formula (IV) 25 above, mention may be made more particularly of 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-

diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

The diaminopyrazole(s) and/or the

5 triaminopyrazole(s) in accordance with the invention
and/or the corresponding addition salt(s) with an acid
preferably represent(s) from 0.0005 to 12% by weight
approximately relative to the total weight of the dye
composition, and even more preferably from 0.005 to 6%

10 by weight approximately relative to this weight.

The halogenated meta-aminophenol(s) of
formula (I) in accordance with the invention and/or the
corresponding addition salt(s) with an acid preferably
represent(s) from 0.0001 to 5% by weight approximately
15 relative to the total weight of the dye composition,
and even more preferably from 0.005 to 3% by weight
approximately relative to this weight.

The dye compositions in accordance with the
invention can contain other couplers conventionally
20 used for oxidation dyeing, other than the halogenated
meta-aminophenols of formula (I), and/or other
oxidation bases conventionally used for oxidation
dyeing, other than a diaminopyrazole and a
triaminopyrazole and/or direct dyes, in particular in
25 order to modify the shades or to enrich them with
glints.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the

5 hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) generally consists of water or of a mixture of water and at least one organic solvent to dissolve the

10 compounds which would not be sufficiently soluble in water. Organic solvents which may be mentioned, for example, are C₁-C₄ lower alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol

15 monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, as well as aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

The solvents can be present in proportions

20 preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

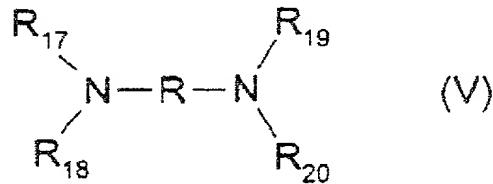
The pH of the dye composition in accordance

25 with the invention is generally between 3 and 12 approximately and even more preferably between 5 and 11

approximately. It can be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres.

Among the acidifying agents which may be 5 mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, carboxylic acids such as tartaric acid, citric acid and lactic acid, and sulphonic acids.

Among the basifying agents which may be 10 mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (V) below:



in which R is a propylene residue optionally substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R₁₇, R₁₈, R₁₉ and R₂₀, which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or 20 C₁-C₄ hydroxyalkyl radical.

The dye composition according to the invention can also contain various adjuvants conventionally used in compositions for dyeing the

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hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic

5 thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersants, conditioners such as, for example, volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and

10 opacifiers.

Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s) such that the advantageous properties intrinsically associated with the

15 combination in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

The dye composition according to the invention can be in various forms, such as in the form

20 of liquids, creams or gels or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

A subject of the invention is also a process for dyeing keratin fibres, and in particular human

25 keratin fibres such as the hair, using the dye composition as defined above.

According to this process, the dye composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH with the aid of an oxidizing agent which is 5 added to the dye composition just at the time of use, or which is present in an oxidizing composition that is applied simultaneously or sequentially.

According to one particularly preferred embodiment of the dyeing process according to the 10 invention, the dye composition described above is mixed, at the time of use, with an oxidizing composition containing, in a medium which is suitable for dyeing, at least one oxidizing agent present in an amount which is sufficient to develop a coloration. The 15 mixture obtained is then applied to the keratin fibres and is left to stand on them for 3 to 60 minutes approximately, preferably 5 to 40 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

20 The oxidizing agent present in the oxidizing composition as defined above can be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali 25 metal bromates, persalts such as perborates,

percarbonates and persulphates, and peracids. Hydrogen peroxide is particularly preferred.

The pH of the oxidizing composition containing the oxidizing agent as defined above is such 5 that after mixing with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately and even more preferably between 5 and 11. It is adjusted to the desired value by means of acidifying or 10 basifying agents usually used in the dyeing of keratin fibres and as defined above.

The oxidizing composition as defined above can also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined 15 above.

The composition which is finally applied to the keratin fibres can be in various forms, such as in the form of liquids, creams or gels or in any other form which is suitable for dyeing keratin fibres, and 20 in particular human hair.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains the dye composition as defined above, 25 and a second compartment of which contains the oxidizing composition as defined above. These devices

can be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

The examples which follow are intended to 5 illustrate the invention without, however, limiting its scope.

EXAMPLES

COMPARATIVE DYEING EXAMPLES 1 TO 4

The dye compositions below, in accordance 10 with the invention, were prepared (contents in grams):

EXAMPLE	1 (*)	2	3	4
4,5-diamino-1-ethyl-3-methylpyrazole dihydrochloride (oxidation base)	0.639	0.639	0.639	0.639
3-aminophenol (coupler not forming part of the invention)	0.327	-	-	-
3-amino-6-chlorophenol (coupler in accordance with the invention)	-	0.431	-	-
3-(β -aminoethyl)amino-6-chlorophenol (coupler in accordance with the invention)	-	-	0.560	-

EXAMPLE	1 (*)	2	3	4
3 - (β-hydroxyethyl) amino-6- chlorophenol (coupler in accordance with the invention)	-	-	-	0.563
Common dye support	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

(*) : example not forming part of the invention

(**) common dye support:

- Oleyl alcohol polyglycerated with 4.0 g
- 2 mol of glycerol
- Oleyl alcohol polyglycerated with 5.69 g A.M.
- 4 mol of glycerol, containing 78% active
- material (A.M.)
- Oleic acid 3.0 g
- Oleylamine containing 2 mol of 7.0 g
- ethylene oxide, sold under the tradename
- Ethomeen O12® by the company Akzo
- Diethylaminopropyl lauryl amino 3.0 g A.M.
- succinamate, sodium salt, containing
- 55% A.M.
- Oleyl alcohol 5.0 g
- Oleic acid diethanolamide 12.0 g
- Propylene glycol 3.5 g
- Ethyl alcohol 7.0 g

- Dipropylene glycol	0.5 g
- Propylene glycol monomethyl ether	9.0 g
- Sodium metabisulphite as an aqueous solution containing 35% A.M.	0.455 g A.M.
- Ammonium acetate	0.8 g
- Antioxidant, sequestering agent	q.s.
- Fragrance, preserving agent	q.s.
- Aqueous ammonia containing 20% NH ₃	10 g

It is important to note that each of the dye compositions 1 to 4 above contains the same molar amount of coupler, i.e. 3×10^{-3} mol.

5 At the time of use, each dye composition above was mixed with an equal amount by weight of an oxidizing composition consisting of a 20-volumes aqueous hydrogen peroxide solution (6% by weight).

10 Each resulting composition was applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

The locks of dyed hair were then subjected to a test of resistance to the action of perspiration.

15 The colour of the locks of hair dyed with compositions 1 to 4 was evaluated in the Munsell system using a Minolta® CM 2002 colorimeter, before the test of resistance to the action of perspiration.

According to the Munsell notation, a colour is defined by the expression H V / C in which the three parameters respectively denote the shade or Hue (H), the intensity or Value (V) and the purity or 5 Chromaticity (C), the oblique line in this expression simply being a convention and not indicating a ratio.

The locks of dyed hair were then subjected to the test of resistance to the action of perspiration.

To do this, the locks of dyed hair were 10 immersed in a crystallizing dish covered with a watch glass and containing a solution of synthetic sweat of the following composition:

- NaCl	1.0 g
- Potassium hydrogen phosphate	0.1 g
15 - Histidine	0.025 g
- Lactic acid qs	pH 3.2
- Distilled water qs	100 g

The locks of dyed hair were left to stand in 20 this synthetic sweat solution for 48 hours at 37°C. The locks were then rinsed, followed by drying.

The colour of the locks was then re-evaluated in the Munsell system using a Minolta® CM 2002 colorimeter.

25 The difference between the colour of the lock before the test of resistance to perspiration and the

colour of the lock after the test of resistance to perspiration was calculated by applying the Nickerson formula

$$\Delta E = 0.4C_0dH + 6dV + 3dC$$

5 as described, for example, in "Couleur, Industrie et Technique [Colour, Industry and Technique]"; pages 14-17; vol. No 5; 1978.

In this formula, ΔE represents the difference in colour between two locks, ΔH , ΔV and ΔC represent 10 the variation in absolute value of the parameters H , V and C , and C_0 represents the purity of the lock relative to which it is desired to evaluate the colour difference.

The degradation of the colour is 15 proportionately greater the larger the value of ΔE .

The results are given in the table below:

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EXAMPLE	Colour of the hair before the test	Colour of the hair after the test	Degradation of the colour			
			ΔH	ΔV	ΔC	ΔE
1 (*)	9.2 RP 3/3/2.6	2.5 YR 3.9/2.1	13.3	0.6	0.5	18.9
2	2.6 RP 3.0/3.7	6.1 RP 3.5/3.2	3.5	0.5	0.5	9.7
3	2.6 RP 3.0/2.9	4.1 RP 3.0/2.9	1.5	0	0	1.7
4	2.7 RP 3.2/3.2	6.1 RP 3.5/3.0	3.4	0.3	0.2	6.8

These results show that the coloration obtained using the dye composition of Example 1 not forming part of the invention, since it contains a combination of a diaminopyrazole and a non-halogenated meta-aminophenol, is markedly less resistant to the action of perspiration than the colorations obtained using the compositions of Examples 2 to 4, all of which form part of the invention since they contain a combination of a diaminopyrazole and a meta-aminophenol which is halogenated ortho to the phenol.

DYEING EXAMPLES 5 TO 8

The dye compositions below, in accordance with the invention, were prepared (contents in grams):

EXAMPLE	5	6	7	8
4,5-diaminopyrazole di-hydrochloride (oxidation base)	0.513	-	-	-
1-methyl-4,5-diaminopyrazole dihydrochloride (oxidation base)	-	0.555	0.555	0.555
3-amino-2-chloro-6-methylphenol (coupler in accordance with the invention)	0.473	0.473	-	-
3-amino-6-chlorophenol (coupler in accordance with the invention)	-	-	0.431	-
3-(β -aminoethyl)amino-6-chlorophenol (coupler in accordance with the invention)	-	-	-	0.560
Common dye support	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

5 (***) common dye support:

This is identical to the one used for Examples 1 to 4 above.

At the time of use, each dye composition 5 above was mixed with an equal amount by weight of an oxidizing composition consisting of a 20-volumes aqueous hydrogen peroxide solution (6% by weight).

Each resulting composition was applied for 30 minutes to locks of natural grey hair containing 90% 10 white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

The locks were dyed in the shades given in the table below:

EXAMPLE	SHADE OBTAINED
5	Red-coppery
6	Red-coppery
7	Red-iridescent
8	Iridescent red

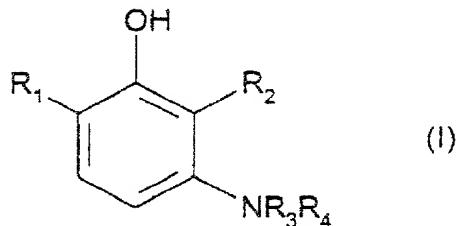
CLAIMS

1. Composition for the oxidation dyeing of human keratin fibres and in particular human keratin fibres such as the hair, characterized in that it

5 comprises, in a medium which is suitable for dyeing:

- at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles;
- and at least one coupler chosen from the halogenated meta-aminophenols of formula (I) below, and the

10 addition salts thereof with an acid:



in which:

- R₁ and R₂, which may be identical or different, represent a hydrogen atom, a halogen atom such as

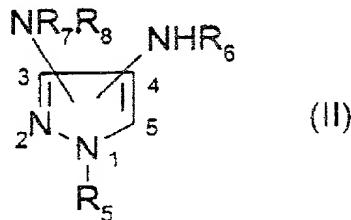
15 chlorine, bromine, iodine or fluorine, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkoxy radical or a C₂-C₄ polyhydroxyalkoxy radical;

- R₃ and R₄, which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical or a C₁-C₄ monoaminoalkyl radical;

it being understood that at least one of the radicals R_1 and R_2 represents a halogen atom.

2. Composition according to Claim 1,
 characterized in that the halogenated meta-aminophenols
 5 of formula (I) are chosen from 3-amino-6-chlorophenol,
 3-amino-6-bromophenol, 3-(β -aminoethyl)amino-6-
 chlorophenol, 3-(β -hydroxyethyl)amino-6-chlorophenol
 and 3-amino-2-chloro-6-methylphenol, and the addition
 salts thereof with an acid.

10 3. Composition according to Claim 1 or 2,
 characterized in that the diaminopyrazoles which can be
 used as oxidation bases are chosen from:
 a) the diaminopyrazoles of formula (II) below, and the
 addition salts thereof with an acid:



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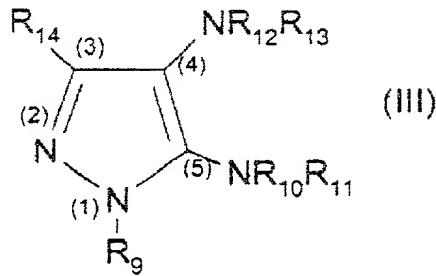
in which:

- R_5 represents a hydrogen atom, a C_1 - C_6 alkyl radical,
 a C_2 - C_4 hydroxyalkyl radical, a benzyl radical, a phenyl
 radical, a benzyl radical substituted with a halogen
 20 atom or with a C_1 - C_4 alkyl or C_1 - C_4 alkoxy group, or
 forms, with the nitrogen atom of the group NR_7R_8 in
 position 5, a hexahdropyridazine or tetrahydropyrazole

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heterocycle which is optionally monosubstituted with a C₁-C₄ alkyl group;

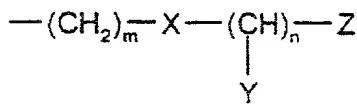
- R₆ and R₇ which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, a C₂-C₄ hydroxyalkyl radical, a benzyl radical or a phenyl radical;
- R₈ represents a hydrogen atom, or a C₁-C₆ alkyl or C₂-C₄ hydroxyalkyl radical; with the proviso that R₆ represents a hydrogen atom when R₅ represents a substituted benzyl radical or forms a heterocycle with the nitrogen atom of the group NR₇R₈ in position 5;
- 10 b) the diaminopyrazoles of formula (III) below, and the addition salts thereof with an acid:



- 15 in which:

- R₉, R₁₀, R₁₁, R₁₂ and R₁₃, which may be identical or different, represent a hydrogen atom; a linear or branched C₁-C₆ alkyl radical; a C₂-C₄ hydroxyalkyl radical; a C₂-C₄ aminoalkyl radical; a phenyl radical; a phenyl radical substituted with a halogen atom or a C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, trifluoromethyl, amino or C₁-C₄ alkylamino radical; a benzyl radical; a benzyl

radical substituted with a halogen atom or with a C₁-C₄ alkyl, C₁-C₄ alkoxy, methylenedioxy or amino radical; or a radical



5 in which m and n are integers, which may be identical or different, between 1 and 3 inclusive, X represents an oxygen atom or an NH group, Y represents a hydrogen atom or a methyl radical, and Z represents a methyl radical, a group OR or NRR' in which R and R', which

10 may be identical or different, denote a hydrogen atom, a methyl radical or an ethyl radical, it being understood that when R₁₀ represents a hydrogen atom, then R₁₁ can also represent an amino or C₁-C₄ alkylamino radical,

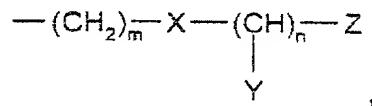
15 - R₁₄ represents a linear or branched C₁-C₆ alkyl radical; a C₁-C₄ hydroxyalkyl radical; a C₁-C₄ aminoalkyl radical; a (C₁-C₄)alkylamino(C₁-C₄)alkyl radical; a di(C₁-C₄)alkylamino(C₁-C₄)alkyl radical; a hydroxy(C₁-C₄)alkylamino(C₁-C₄)alkyl radical; a (C₁-C₄)alkoxymethyl

20 radical; a phenyl radical; a phenyl radical substituted with a halogen atom or with a C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, trifluoromethyl, amino or C₁-C₄ alkylamino radical; a benzyl radical; a benzyl radical substituted with a halogen atom or with a C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, trifluoromethyl, amino or C₁-C₄ alkylamino

25

radical, a heterocycle chosen from thiophene, furan and pyridine, or alternatively a radical $-(CH_2)_p-O-(CH_2)_q-$ OR", in which p and q are integers, which may be identical or different, between 1 and 3 inclusive, and

5 R" represents a hydrogen atom or a methyl radical,
it being understood that, in formula (III) above,
- at least one of the radicals R₁₀, R₁₁, R₁₂ and R₁₃
represents a hydrogen atom,
- when R₁₀, or R₁₂, respectively, represents a
10 substituted or unsubstituted phenyl radical, or a
benzyl radical or a radical



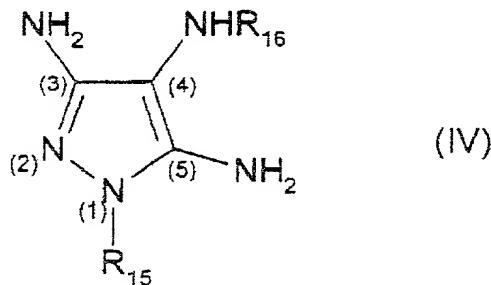
then R_{11} , or R_{13} , respectively, cannot represent any of these three radicals.

15 - when R_{12} and R_{13} simultaneously represent a hydrogen atom, then R_9 can form, with R_{10} and R_{11} , a hexahydropyrimidine or tetrahydroimidazole heterocycle which is optionally substituted with a C_1 - C_4 alkyl or 1,2,4-tetrazole radical,

20 - when R_{10} , R_{11} , R_{12} and R_{13} represent a hydrogen atom or a C_1 - C_6 alkyl radical, then R_9 or R_{14} can also represent a 2-, 3- or 4-pyridyl, 2- or 3-thienyl or 2- or 3-furyl heterocyclic residue which is optionally substituted

with a methyl radical or alternatively a cyclohexyl radical.

4. Composition according to Claim 1 or 2, characterized in that the triaminopyrazoles which can 5 be used as oxidation bases are chosen from the compounds of formula (IV) below, and the addition salts thereof with an acid:



in which:

10 - R₁₅ and R₁₆, which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₂-C₄ hydroxyalkyl radical.

5. Composition according to Claim 3, characterized in that the diaminopyrazoles of formula 15 (II) are chosen from 4,5-diamino-1-(4'-methoxybenzyl)-pyrazole, 4,5-diamino-1-(4'-methylbenzyl)pyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1-(3'-methoxybenzyl)pyrazole, 4-amino-1-(4'-methoxybenzyl)-5-methylaminopyrazole, 4-amino-5-(β-hydroxyethyl)amino-1-(4'-methoxybenzyl)pyrazole, 4-amino-5-(β-hydroxyethyl)-amino-1-methylpyrazole, 4-amino-(3)5-methylamino-

pyrazole, 3-(5)4-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-benzylpyrazole, 3-amino-4,5,7,8-tetrahydropyrazolo[1,5-a]pyrimidine, 7-amino-2,3-dihydro-1H-imidazolo[1,2-b]pyrazole and 3-amino-8-5-methyl-4,5,7,8-tetrahydropyrazolo[1,5-a]pyrimidine, and the addition salts thereof with an acid.

6. Composition according to Claim 3, characterized in that the diaminopyrazoles of formula (III) are chosen from:

10 - 1-benzyl-4,5-diamino-3-methylpyrazole,
 - 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methoxyphenyl)-pyrazole,
 - 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methylphenyl)-pyrazole,

15 - 4,5-diamino-1-(β -hydroxyethyl)-3-(3'-methylphenyl)-pyrazole,
 - 4,5-diamino-3-methyl-1-isopropylpyrazole,
 - 4,5-diamino-3-(4'-methoxyphenyl)-1-isopropylpyrazole,
 - 4,5-diamino-1-ethyl-3-methylpyrazole,

20 - 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
 - 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-tert-butylpyrazole,

25 - 4,5-diamino-3-hydroxymethyl-1-phenylpyrazole,

- 4,5-diamino-3-hydroxymethyl-1-(2'-methoxyphenyl)-pyrazole,
- 4,5-diamino-3-hydroxymethyl-1-(3'-methoxyphenyl)-pyrazole,
- 5 - 4,5-diamino-3-hydroxymethyl-1-(4'-methoxyphenyl)-pyrazole,
 - 1-benzyl-4,5-diamino-3-hydroxymethylpyrazole,
 - 4,5-diamino-3-methyl-1-(2'-methoxyphenyl)pyrazole,
 - 4,5-diamino-3-methyl-1-(3'-methoxyphenyl)pyrazole,
- 10 - 4,5-diamino-3-methyl-1-(4'-methoxyphenyl)pyrazole,
 - 3-aminomethyl-4,5-diamino-1-methylpyrazole,
 - 3-aminomethyl-4,5-diamino-1-ethylpyrazole,
 - 3-aminomethyl-4,5-diamino-1-isopropylpyrazole,
 - 3-aminomethyl-4,5-diamino-1-tert-butylpyrazole,
- 15 - 4,5-diamino-3-dimethylaminomethyl-1-methylpyrazole,
 - 4,5-diamino-3-dimethylaminomethyl-1-isopropylpyrazole,
 - 4,5-diamino-3-dimethylaminomethyl-1-tert-butylpyrazole,
- 20 - 4,5-diamino-3-ethylaminomethyl-1-methylpyrazole,
 - 4,5-diamino-3-ethylaminomethyl-1-ethylpyrazole,
 - 4,5-diamino-3-ethylaminomethyl-1-isopropylpyrazole,
 - 4,5-diamino-3-ethylaminomethyl-1-tert-butylpyrazole,
 - 4,5-diamino-3-methylaminomethyl-1-methylpyrazole,
- 25 - 4,5-diamino-3-methylaminomethyl-1-isopropylpyrazole,
 - 4,5-diamino-1-ethyl-3-methylaminomethylpyrazole,

- 1-tert-butyl-4,5-diamino-3-methylaminomethylpyrazole,
- 4,5-diamino-3-[(β -hydroxyethyl)aminomethyl]-1-methylpyrazole,
- 4,5-diamino-3-[(β -hydroxyethyl)aminomethyl]-1-5 isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-[(β -hydroxyethyl)aminomethyl]-pyrazole,
- 1-tert-butyl-4,5-diamino-3-[(β -hydroxyethyl)amino-10 methyl]pyrazole,
- 10 - 4-amino-5- (β -hydroxyethyl) amino-1,3-dimethylpyrazole,
- 4-amino-5- (β -hydroxyethyl) amino-1-isopropyl-3-methylpyrazole,
- 4-amino-5- (β -hydroxyethyl) amino-1-ethyl-3-methylpyrazole,
- 15 - 4-amino-5- (β -hydroxyethyl) amino-1-tert-butyl-3-methylpyrazole,
- 4-amino-5- (β -hydroxyethyl) amino-1-phenyl-3-methylpyrazole,
- 4-amino-5- (β -hydroxyethyl) amino-1- (2-methoxyphenyl)-20 3-methylpyrazole,
- 4-amino-5- (β -hydroxyethyl) amino-1- (3-methoxyphenyl)-3-methylpyrazole,
- 4-amino-5- (β -hydroxyethyl) amino-1- (4-methoxyphenyl)-3-methylpyrazole,

0946338 - 4-amino-5-(β -hydroxyethyl)amino-1-benzyl-3-methylpyrazole,

10 - 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,

15 - 4-amino-1-tert-butyl-3-methyl-5-methylaminopyrazole,

20 - 4,5-diamino-1,3-dimethylpyrazole,

25 - 4,5-diamino-3-tert-butyl-1-methylpyrazole,

30 - 4,5-diamino-1-tert-butyl-3-methylpyrazole,

35 - 4,5-diamino-1-methyl-3-phenylpyrazole,

40 - 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,

45 - 4,5-diamino-1-(β -hydroxyethyl)-3-phenylpyrazole,

50 - 4,5-diamino-1-methyl-3-(2'-chlorophenyl)pyrazole,

55 - 4,5-diamino-1-methyl-3-(4'-chlorophenyl)pyrazole,

60 - 4,5-diamino-1-methyl-3-(3'-trifluoromethylphenyl)pyrazole,

65 - 4,5-diamino-1,3-diphenylpyrazole,

70 - 4,5-diamino-3-methyl-1-phenylpyrazole,

75 - 4-amino-1,3-dimethyl-5-phenylaminopyrazole,

80 - 4-amino-1-ethyl-3-methyl-5-phenylaminopyrazole,

85 - 4-amino-1,3-dimethyl-5-methylaminopyrazole,

90 - 4-amino-3-methyl-1-isopropyl-5-methylaminopyrazole,

95 - 4-amino-3-isobutoxymethyl-1-methyl-5-methylamino-pyrazole,

100 - 4-amino-3-methoxyethoxymethyl-1-methyl-5-methylamino-pyrazole,

105 - 4-amino-3-hydroxymethyl-1-methyl-5-methylamino-pyrazole,

- 4-amino-1,3-diphenyl-5-phenylaminopyrazole,
- 4-amino-3-methyl-5-methylamino-1-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
- 5-amino-3-methyl-4-methylamino-1-phenylpyrazole,
- 5 - 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-(4'-chlorophenyl)pyrazole;
- 5-amino-3-ethyl-1-methyl-4-(N,N-methylphenyl)amino-pyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-
- 10 phenylpyrazole,
 - 5-amino-3-ethyl-4-(N,N-methylphenyl)aminopyrazole,
 - 5-amino-4-(N,N-methylphenyl)amino-3-phenylpyrazole,
 - 5-amino-4-(N,N-methylphenyl)amino-3-(4'-methyl-phenyl)pyrazole,
- 15 - 5-amino-3-(4'-chlorophenyl)-4-(N,N-methylphenyl)-aminopyrazole,
- 5-amino-3-(4'-methoxyphenyl)-4-(N,N-methylphenyl)-aminopyrazole,
- 4-amino-5-methylamino-3-phenylpyrazole,
- 20 - 4-amino-5-ethylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-(4'-methylphenyl)pyrazole,
- 4-amino-3-phenyl-5-propylaminopyrazole,
- 4-amino-5-butylamino-3-phenylpyrazole,
- 4-amino-3-phenyl-5-phenylaminopyrazole,
- 25 - 4-amino-5-benzylamino-3-phenylpyrazole,
- 4-amino-5-(4'-chlorophenyl)amino-3-phenylpyrazole,

- 4-amino-3-(4'-chlorophenyl)-5-phenylaminopyrazole,
- 4-amino-3-(4'-methoxyphenyl)-5-phenylaminopyrazole,
- 1-(4'-chlorobenzyl)-4,5-diamino-3-methylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,

5 - 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,

- 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

and the addition salts thereof with an acid.

7. Composition according to Claim 6,
characterized in that the diaminopyrazoles of formula
10 (III) are chosen from:

- 4,5-diamino-1,3-dimethylpyrazole,
- 4,5-diamino-3-methyl-1-phenylpyrazole,
- 4,5-diamino-1-methyl-3-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,

15 - 1-benzyl-4,5-diamino-3-methylpyrazole,

- 4,5-diamino-3-tert-butyl-1-methylpyrazole,
- 4,5-diamino-1-tert-butyl-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
- 4,5-diamino-1-ethyl-3-methylpyrazole,

20 - 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,

- 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
- 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
- 4,5-diamino-3-methyl-1-isopropylpyrazole,

25 - 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

and the addition salts thereof with an acid.

8. Composition according to Claim 4

characterized in that the triaminopyrazoles of formula (IV) are chosen from 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-5-methylaminopyrazole and 3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

9. Composition according to any one of the preceding claims, characterized in that the 10 diaminopyrazole(s) and/or the triaminopyrazole(s) and/or the corresponding addition salt(s) with an acid represent(s) from 0.0005 to 12% by weight relative to the total weight of the dye composition.

10. Composition according to Claim 9, 15 characterized in that the diaminopyrazole(s) and/or the triaminopyrazole(s) and/or the corresponding addition salt(s) with an acid represent(s) from 0.005 to 6% by weight relative to the total weight of the dye composition.

20 11. Composition according to any one of the preceding claims, characterized in that the halogenated meta-aminophenol(s) of formula (I) and/or the corresponding addition salt(s) with an acid represent(s) from 0.0001 to 5% by weight relative to 25 the total weight of the dye composition.

12. Composition according to Claim 11,
characterized in that the halogenated meta-
aminophenol(s) of formula (I) and/or the corresponding
addition salt(s) with an acid represent(s) from 0.005
5 to 3% by weight relative to the total weight of the dye
composition.

13. Composition according to any one of the
preceding claims, characterized in that the addition
salts with an acid are chosen from the hydrochlorides,
10 hydrobromides, sulphates, tartrates, lactates and
acetates.

14. Composition according to any one of the
preceding claims, characterized in that the medium
which is suitable for dyeing (or support) consists of
15 water or of a mixture of water and at least one organic
solvent chosen from C₁-C₄ lower alkanols, glycerol,
glycols and glycol ethers, aromatic alcohols, similar
products and mixtures thereof.

15. Composition according to any one of the
20 preceding claims, characterized in that it has a pH of
between 3 and 12.

16. Composition according to any one of the
preceding claims, characterized in that it is in the
form of liquids, creams or gels or in any other form
25 which is suitable for dyeing keratin fibres, and in
particular human hair.

17. Process for dyeing keratin fibres, and
in particular human keratin fibres such as the hair,
characterized in that at least one dye composition as
defined in any one of Claims 1 to 16 is applied to
5 these fibres, and in that the colour is developed at
acidic, neutral or alkaline pH with the aid of an
oxidizing agent which is added to the dye composition
just at the time of use, or which is present in an
oxidizing composition that is applied simultaneously or
10 sequentially.

18. Process according to Claim 17,
characterized in that the oxidizing agent present in
the oxidizing composition is chosen from hydrogen
peroxide, urea peroxide, alkali metal bromates,
15 persalts such as perborates, percarbonates and
persulphates, and peracids.

19. Multi-compartment device or multi-
compartment dyeing "kit", a first compartment of which
contains a dye composition as defined in any one of
20 Claims 1 to 16, and a second compartment of which
contains an oxidizing composition.

ABSTRACT

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,
COMPRISING A DIAMINOPYRAZOLE OR A TRIAMINOPYRAZOLE AND
A HALOGENATED META-AMINOPHENOL, AND DYEING PROCESS

The present invention relates to a composition for the oxidation dyeing of keratin fibres, in particular human keratin fibres such as the hair, comprising at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles, in combination with at least one meta-aminophenol which is halogenated ortho to the phenol, as coupler, and to the dyeing process using this composition with an oxidizing agent.

1. *Leucosia* (L.) *leucostoma* (L.) *leucostoma* (L.) *leucostoma* (L.) *leucostoma* (L.)

Declaration and Power of Attorney for Patent Application

Déclaration et Pouvoir pour Demand de Brevet

French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:

a été déposée le _____
sous le numéro de demande des Etats-Unis ou le _____
numéro de demande international PCT _____
et modifiée _____
(les cas échéant).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnaiss devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

DYEING COMPOSITION FOR KERATIN FIBRES

the specification of which is attached hereto unless the following box is checked:

was filed on July 20, 1998 as United States Application Number or PCT International Application Number PCT/FR98/01591 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)
Demande(s) de brevet antérieure(s)

97/10857 (Number) (Numéro)	France (Country) (Pays)
_____ (Number) (Numéro)	_____ (Country) (Pays)

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International Application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed
Droit de priorité non revendiqué

1 September 1997 (Day/Month/Year Filed) (Jour/Mois/Anné de dépôt)	<input type="checkbox"/>
_____ (Day/Month/Year Filed) (Jour/Mois/Anné de dépôt)	<input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose any or all information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)
(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont laquelle est devenue disponible entre la date de dépôt de la demande antérieure, et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)
(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec L'Office des brevets et des marques: *(mentionner le nom et le numéro d'enregistrement)*.



POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this patent application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)*:

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